Theoretical STM Characterization Of On-surface Reactions Of Heteroaromatics

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Understanding the interaction between organic molecules and surfaces is of paramount importance in diverse fields such as organic electronics, molecular electronics, catalysis, and surface photochemistry, among others. In particular, the bottom-up approach aims at forming tailored nanoarchitectures by manipulating organic molecules at atomic level and it is one of the most effective strategies used in nanotechnology. Catalytic surfaces are often used to prompt a particular reaction as they are very successful in modifying a particular molecule in selected ways. For example, transition metal surfaces are very efficient catalysts of dehydrogenation reactions in Polycyclic Aromatic Hydrocarbon (PAH), usually upon thermal activation. They can act in different ways, depending on the strength of the interaction between the surface and the adsorbate [1]. When a PAH is deposited on a reactive surface, such as Pt(111), the molecule does not diffuse, so the as-deposited molecule sticks where it lands. When this system is annealed, the molecule dehydrogenates which results in an intramolecular transformation, as no intermolecular interaction is allowed as the molecules do not “see” each other. An adequate combination of first-principles calculations, including vdW interactions, with an accurate theoretical STM imaging approach based on the Keldish-Green formalism [2], permits the monitoring and full characterization of the different intermediate steps along the whole thermal-induced dehydrogenation process [1]. Following this line, our research group has recently shown the catalytic properties of the TiO2 (110)-(1×1) surface towards dehydrogenation of large organic molecules [3]. In this case, we have deposited C60H30 molecules on this surface and we have proven that high temperature annealing leads to partial cyclodehydrogenation, which allows the use of the activated PAHs as building blocks for larger nanostructures. In this way, the formation of fullerene-like nanodomes on this dielectric surface was observed by STM. The different stages of this on-surface chemistry were followed by different experimental techniques (STM, XPS and NEXAFS), and fully characterized by the mentioned theoretical framework. For this particular interface, theory shed some light on the origin of the two different sets of molecules observed in the UHV-STM images, one vanishing for certain values of the external tunnelling bias, and the other set of molecules observed at all range of bias, which is directly related to the dehydrogenation stage of the molecules [3].

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